

# **AB 32 and the California Petroleum Refinery Sector**

## **Greenhouse Gas Inventory & Reporting**

### **Technical Discussion**



**May 22, 2007  
Sacramento**

# Discussion Topics

- Emissions Inventory and 1990 Level
  - Objectives, Estimates, Update Approach
- Mandatory Reporting
  - Basics and Boundaries
  - Stationary Combustion
  - Process Emissions
  - Fugitive Emissions
  - Mobile Emissions
  - Additional Sources, Methods, Gases
  - Next Steps

# Emissions Inventory Objectives

- Meet requirements of AB 1803 and AB 32
- By January 1, 2008
  - Review, document, and update statewide GHG emissions inventory for 1990-2004
  - Determine 1990 statewide GHG emissions level
  - Establish 2020 GHG emissions limit (equivalent to 1990 emissions level)

# Existing Emissions Estimates for the Refinery Sector

- Refinery sector estimate for 1990: 27.85 MMTCO<sub>2</sub>e
- Estimate based on fuel consumed
  - Refinery gas
  - Natural gas
  - LPG
  - Distillate
  - Residual oil
  - Petroleum coke

# Data Sources

- Energy Information Administration
- CEC (Petroleum Industry Information & Reporting Act)
- California Refineries

# Approach for Updating Refinery Sector Estimates

- Default
  - Existing CEC estimates for refinery sector emissions 1990-2004
  - Existing refinery sector contribution in determining 1990 emission level and 2020 limit
- Use facility-specific data, if possible
  - Reconcile existing top-down estimates with facility data from 21 refineries

# Schedule

- Additional discussions
  - On-going
- Staff report
  - Initial draft anticipated in late summer
- Presentation to ARB Board in late 2007
  - Emissions Inventory (1990-2004)
  - 1990 Level & 2020 Limit

# Proposed Reporting Basics

- Annual reporting on a facility basis
- Stationary combustion, process, fugitive emissions (direct emissions)
- Facility (on-site) mobile sources if significant
- Purchased energy usage (indirect emissions)
- All 6 Kyoto gases -- unless methods not specified in the regulation

# Defining the Facility

- Sources on contiguous or adjacent property
- Under common operational control
  - Authority to implement environmental, health, safety rules
- Physical boundary (fenceline)

# Stationary Combustion Emissions Carbon Dioxide

## Addressing Refinery Fuel Variability

Refinery Fuel Composition Can Be Highly Variable

Therefore, the chemical composition and/or HHV of refinery fuel must be well characterized

Where in the process stream is refinery gas currently sampled? Are additional sampling points needed?

What sampling frequency is necessary to insure accurate emissions determinations? Daily, weekly, monthly?

Minimum determination is HHV. Periodically, the Carbon content should be determined and used to check the accuracy of HHV based calculations

# Stationary Combustion CO<sub>2</sub> Emissions Refinery Fuel

## Carbon Content – Preferred Methodology

$$F(\text{m}^3/\text{unit time}) \times CF(\text{gmole}/\text{m}^3) \times M(\text{g}/\text{gmole}) \times \\ C(\text{g C}/\text{g fuel}) \times 44\text{g CO}_2/12 \text{ g C} \times \text{Mt}/10^6\text{g}$$

## HHV – Alternative Methodology

$$F(\text{scf}/\text{unit time}) \times \text{HHV}(\text{Btu}/\text{scf}) \times \text{EF}(\text{tonnes C}/10^6 \text{ Btu}) \times 44 \text{ g CO}_2/12 \text{ g C}$$

Areas of concern: use of refinery fuel as feedstock for boilers, heaters, H<sub>2</sub> production, etc.

ASTM Methods will be applied to HHV and flow rate determination

# Stationary Combustion CO<sub>2</sub> Emissions

## Natural Gas, LPG, other gases

- **Preferred approach**

Carbon Fraction or Energy Content (HHV) measured –  
provided by fuel supplier or refinery lab

- **Alternative Approach**

Assumed or default heating value

HHV determined periodically to verify that the fuel HHV  
is within tolerance limits for accuracy purposes

(e.g. NG: 975 – 1100 Btu/scf)

LPG – default values for unspecified LPG or pure  
compounds acceptable

Refinery LPG must be characterized (CF and/or HHV)

# Stationary Combustion CH<sub>4</sub> and N<sub>2</sub>O Emissions

## Possible Emissions Estimation Methods

- Unit specific emission factors
- Default emission factors (EIA, EPA AP-42, IPCC)
  - Refinery Gas – API equipment specific EFs

# Process Emissions

## Catalytic Cracking Units (CO<sub>2</sub>)

### (1) Coke Burned Method

USEPA 40 Part 63 (40CFR63.1564) refineries calculate coke burn rate (Rc)

$$ECO_2 = Rc \times CF \times [44 \text{ mass units of CO}_2 / 12 \text{ Mass units of C}]$$

### (2) Air rates and flue gas CO/CO<sub>2</sub> based method

$$ECO_2 = (AR + SOR) \times (FCO_2 + FCO) \times 44 / \text{molar conversion factor} \times 525,600 \text{ min/yr}$$

CF = coke carbon fraction

AR = air rate to regenerator

SOR = supplemental O<sub>2</sub> rate

FCO<sub>2</sub> = fraction of CO<sub>2</sub> in flue gas

FCO = fraction of CO in flue gas

# Process Emissions

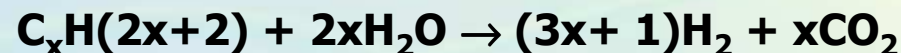
## Catalytic Cracking Units (CO<sub>2</sub>)

- Are site-specific Coke Carbon Fractions (CF) values available?
- Assuming CF = 1 will tend to overestimate CO<sub>2</sub> emissions.
- Is the Coke Burn Rate (R<sub>c</sub>) calculated routinely for all fluid (FCCU) and Flexi-coker units?
- Intermittent Catalyst regeneration.
  - Is the weight fraction of carbon on the spent catalyst known?
  - Is the weight of spent catalyst regenerated known?
  - Is intermittent catalyst regeneration sometimes done off-site?

# Process Emissions

## Hydrogen Plant Production (CO<sub>2</sub>)

**API Preferred Methods – 1) Mass balance or 2) H<sub>2</sub> production rate based  
H<sub>2</sub> production reaction**



**1)  $\text{ECO}_2 = \text{FR} \times \text{CF} \times 44\text{g CO}_2/12\text{g C}$  or**

**2)  $\text{ECO}_2 = \text{H}_2\text{R} \times (x \text{ mole CO}_2)/(3x + 1) \times 44/\text{molar volume conversion}$**

**where:**

<b>FR</b>	<b>= feedstock rate</b>
<b>CF</b>	<b>= carbon fraction (fuel composition)</b>
<b>H<sub>2</sub>R</b>	<b>= hydrogen production rate</b>
<b>X</b>	<b>= stoichiometry derived from feedstock composition</b>

# Process Emissions

## Hydrogen Plant Production (CO<sub>2</sub>)

- What feed stocks variants are used in California refinery hydrogen production plants?
  - Straight NG
  - Natural gas and refinery gas
  - Naphtha
- Is the carbon content of refinery gas and naphtha feed stocks determined?
- Is the mixing ratio of feed stock blends determined accurately?
- How well is the hydrogen production rate (H<sub>2</sub>R) known?
- Emissions from Stripper Vents and PSA stream?

# **Process Emissions**

## **Sulfur Recovery Units (CO<sub>2</sub>)**

- **Crude derived carbon entrained in the SRU process.**
- **Are data available concerning CO<sub>2</sub> emissions from SRUs?**
- **Is tail gas flow rate measured?**
- **A value of 12% (mole) CO<sub>2</sub> in tail gases has been assumed. Is this reasonable? Is additional data available?**

# Process Data

Data collection, archiving, and validation

- Hydrogen plant operation
- FCCU operation
- Are QA/QC procedures in-place for the sensors, CEMS, flow meters, data collection systems etc ?

# Fugitive Emissions

## Storage Tanks (CH<sub>4</sub>)

Fugitive CH<sub>4</sub> loss from crude oil storage tanks

- Working
- Breathing
- Flashing Losses
  
- Which model or approach is most appropriate?
  - EPA TANKS and AP42 do not estimate flashing losses
  - Simple emission factors (tonnes CH<sub>4</sub>/bbl crude) - overestimate
  
- E&P TANK equation of state estimates all three losses
  - Software available from API (\$450)

# Fugitive Emissions

## Fuel gas system and process equipment leaks ( $\text{CH}_4$ )

- Do all refineries have Leak Detection and Repair (LDAR) programs?
- Are these programs consistent among air districts?  
AQMD?
- Are VOC data available and is there a correlation to  $\text{CH}_4$ ?
- How do we establish emission factors?

# Fugitive Emissions

## Flares ( $\text{CO}_2$ , $\text{CH}_4$ , $\text{N}_2\text{O}$ )

- What data do refineries routinely collect? Does data quality and availability vary with AQMD?

Gas flow rate

Gas composition

- API – no  $\text{CO}_2$  or  $\text{N}_2\text{O}$  emission factors available,  $\text{CH}_4$  scf/1000 bbl refinery feed
- Emissions calculation methods

$$E = F \times EF$$

# Fugitive Emissions

## Uncontrolled Blowdown Units (CH<sub>4</sub>)

- Are there are any uncontrolled blowdown units still operational in California?
- What data are available on volumetric flow rates, feed stock composition?

# Refinery Hazardous Waste (CO<sub>2</sub>)

- K169 – crude oil storage tank sediment
- K170 – clarified slurry oil storage tank sediment
- K171 – spent hydrotreating catalyst
- K172 – spent hydrorefining catalyst
- What disposal methods are used?
  - Incineration – on or off-site?
  - Landfill disposal

# Mobile Source Emissions

## ■ On-Road Vehicles

- Fuel consumption/Vehicle type and model year data
- Fuel consumption/Fuel CO<sub>2</sub> emission factor
- CH<sub>4</sub>, N<sub>2</sub>O vehicle mileage and vehicle EFs or weighted average EFs
- Report biofuels?

## ■ Off-Road Vehicles

- Metered fuel used or bulk fuel purchases and fuel CO<sub>2</sub> emission factors

# Additional Methods

- Refrigerants
  - Propose minimum cut-off (e.g., lbs HFC 134a purchased/year)
  - Simple mass balance calculation method
- Wastewater Treatment
  - BOD/COD model with CH<sub>4</sub> emission factors

# Questions

Are fugitive and mobile emissions significant enough to include?

Additional methodologies required?

Other GHG sources?

General or Specific Concerns?

# Agenda for Next Meeting

- Revisit outstanding questions on combustion and process methods
- Approaches on fugitive and mobile emissions
- Cogeneration
- Energy purchases (indirect emissions)
- Verification
- Other items?

# Steps Ahead

Refinery Technical Discussions

June 19, 2007

July 6, 2007

Mandatory Reporting Workshop

May 23, 2007

Late July / Early August

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